

# Relationship of ozone and carbon monoxide over North America

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**Abstract.** Observations at sites in eastern North America show a strong correlation between  $O_3$  and CO concentrations in summer, with a consistent slope  $\Delta O_3/\Delta CO \approx 0.3$ . Observations in the aged Denver plume at Niwot Ridge, Colorado, also show a strong correlation but with  $\Delta O_3/\Delta CO = 0.15$ . These data offer a sensitive test for evaluating the ability of photochemical models to simulate production of  $O_3$  over North America and its export to the global atmosphere. Application to the Harvard/Goddard Institute for Space Studies three-dimensional, continental-scale model shows that the model gives a good simulation of the observed  $O_3$ -CO correlations and of the associated  $\Delta O_3/\Delta CO$ . This successful simulation lends support to model estimates of  $6 \text{ Gmol d}^{-1}$  for the net  $O_3$  production in the U.S. boundary layer in summer (corresponding to a net  $O_3$  production efficiency of 5.5, which is the number of  $O_3$  molecules produced per molecule of  $NO_x$  consumed) and 70% for the fraction of the net production that is exported to the global atmosphere. Export of U.S. pollution appears to make a significant contribution to total tropospheric  $O_3$  over the northern hemisphere in summer. Simple interpretation of observed  $\Delta O_3/\Delta CO$  as an  $O_3$ /CO anthropogenic enhancement ratio is shown to underestimate substantially anthropogenic  $O_3$  production, because  $O_3$  and CO concentrations are negatively correlated in the absence of photochemistry. It is also shown that concurrent observations of  $\Delta O_3/\Delta CO$  and  $\Delta O_3/\Delta(NO_y - NO_x)$  ratios can be used to impose lower and upper limits on the net  $O_3$  production efficiency.

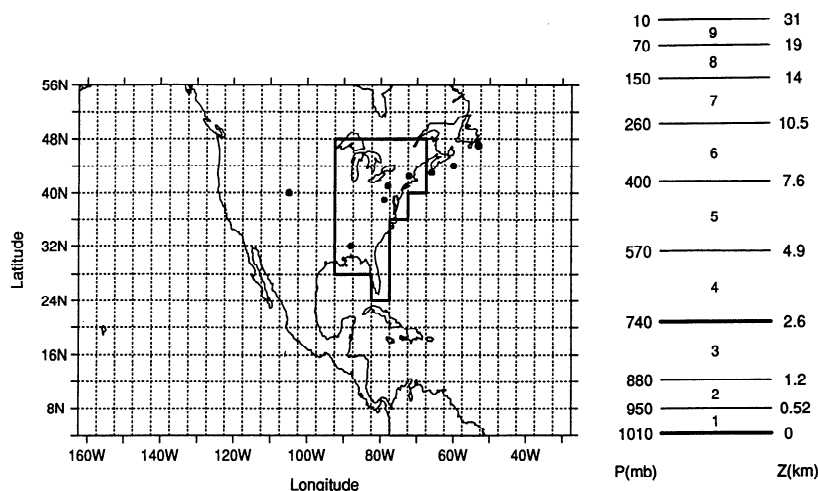
## 1. Introduction

Tropospheric  $O_3$  is a key precursor of the hydroxyl radical which controls the oxidizing power of the atmosphere [Logan *et al.*, 1981; Thompson, 1992]. Ozone is also one of the major pollutants which, in high concentration, can be harmful to human health and to plants. Large amounts of anthropogenic  $O_3$  are produced over the United States in summer by photochemical oxidation of nonmethane hydrocarbons (NMHCs) in the presence of nitrogen oxides ( $NO_x = NO + NO_2$ ). Quantifying this anthropogenic source of  $O_3$  and assessing its global influence is presently a major research issue in tropospheric chemistry [Liu *et al.*, 1987; International Global Atmospheric Chemistry (IGAC), 1992; Parrish *et al.*, 1993].

The covariance of  $O_3$  and CO concentrations offers a valuable constraint for quantifying the anthropogenic source of  $O_3$ . Carbon monoxide is a long-lived tracer of human activity with relatively well known sources from combustion, industry, and oxidation of hydrocarbons [Logan *et al.*, 1981]. Several authors have used the  $O_3$ -CO correlation measured from aircraft downwind of the United States to

diagnose pollution influence on  $O_3$  [Fishman and Seiler, 1983; Fishman *et al.*, 1987; Chameides *et al.*, 1987, 1989; Marengo and Said, 1989]. Recently, Parrish *et al.* [1993] made a first estimate of the export of anthropogenic  $O_3$  from North America to the North Atlantic by using the slope  $\Delta O_3/\Delta CO \approx 0.3$  measured at three Canadian marine sites downwind of the United States and scaling to a CO emission inventory for the eastern United States. They concluded that export of pollution from the United States dominates over transport from the stratosphere as a source of  $O_3$  to the lower troposphere over the North Atlantic in summer.

A more detailed interpretation of  $\Delta O_3/\Delta CO$  in terms of  $O_3$  production requires a three-dimensional model that can resolve complicating factors such as the effect of  $O_3$  deposition, the presence of chemical sources and sinks for CO, and spatial variability. We present here such an analysis using a continental-scale model for  $O_3$  and its precursors over North America [Jacob *et al.*, 1993a]. Our principal objective is to use the  $O_3$ -CO correlation as a test of the ability of the model to compute production of  $O_3$  over the continent. The particular value of this test is that it normalizes  $O_3$  photochemical enhancements to a long-lived tracer of human activity. Ozone concentrations alone do not offer as sensitive a test because they include a substantial and variable background advected from the model boundaries (e.g., from the oceans or from high altitude). In rural surface



**Figure 1.** Model domain and grid. The vertical grid (nine layers) is defined by a sigma coordinate; pressures and altitudes at layer boundaries are shown for an atmospheric column based at sea level. Locations of the measurement sites are indicated by solid circles (see Table 1). The domain enclosed by thick lines and extending from the surface to 2.6 km altitude is the eastern U.S. boundary layer used in the text for budget calculations.

air over the eastern United States, about half of the mean summertime O<sub>3</sub> concentration appears to be contributed by advection from outside North America [Jacob *et al.*, 1993a]. The O<sub>3</sub>-CO correlation removes to a large degree the sensitivity to background. As such, it diagnoses whether the model is giving a successful simulation of O<sub>3</sub> for the right reasons.

Section 2 gives a brief description of the model and summarizes important previous results. Section 3 presents observed O<sub>3</sub>-CO correlations at sites in North America and compares model to observations. Section 4 assesses the possibility for direct interpretation of observed  $\Delta\text{O}_3/\Delta\text{CO}$  as an anthropogenic enhancement ratio. Conclusions are in section 5.

## 2. The Model

The three-dimensional photochemical model of Jacob *et al.* [1993a] covers a domain including North and Central America and large portions of surrounding oceans with 4° latitude × 5° longitude grid resolution and nine vertical layers (Figure 1). Six tracers are transported, including odd oxygen (which is mainly O<sub>3</sub>), CO, NO<sub>x</sub>, peroxyacetyl nitrates (PANs), and two lumped NMHCs. Anthropogenic emissions of NO<sub>x</sub>, CO, and NMHCs in North America are taken from a summer 1985 inventory compiled by the National Acid Precipitation Assessment Program (NAPAP) [Environmental Protection Agency (EPA), 1989]. Biogenic emission of isoprene and dry depositions of O<sub>3</sub>, NO<sub>x</sub>, and PANs, are computed using process models dependent on surface-type and meteorological variables. Chemical reaction rates are computed using the photochemical mechanism of Lurmann *et al.* [1986] with minor modifications [Jacob *et al.*, 1989]. Nonlinear chemistry in urban and industrial plumes is represented with a sub-grid-nested scheme in which concentrated pollution sources are forced to age in isolation for at least 8 hours before being mixed on the grid scale [Sillman *et al.*, 1990a].

The simulation is conducted for 3 summer months (June to

August) with 2 weeks of initialization in May. Meteorological input is provided by one summer of data from a general circulation model (GCM) developed at the Goddard Institute of Space Studies (GISS) [Hansen *et al.*, 1983]. Meteorological variables are updated every 4 hours, and model output is also sampled every 4 hours. Boundary concentrations at the edges of Figure 1 are specified as a function of latitude, altitude, and month using observations.

The GCM is intended to simulate a typical year rather than any particular year; evaluation of model results with observations must therefore focus on seasonal statistics rather than on values for any particular day. Jacob *et al.* [1993a] previously evaluated the model with observed statistics for the concentrations of O<sub>3</sub> and precursors at rural sites in the United States. The model reproduces the observed summer median O<sub>3</sub> concentrations to within 5 ppb in most cases, except in the south central United States where concentrations are overpredicted by 15–20 ppb due in part to insufficient ventilation. Median summertime concentrations of CO are simulated to within 30 ppb at all sites, and the spatial variance of rural CO across the United States is well captured.

A detailed discussion of the O<sub>3</sub> budget in the three-dimensional model is given by Jacob *et al.* [1993b]. The net production rate of O<sub>3</sub> in the U.S. boundary layer (0–2.6 km altitude) averages 6.1 Gmol d<sup>-1</sup> for the 3-month period June to August. The net O<sub>3</sub> production efficiency  $\epsilon_N$  (net number of O<sub>3</sub> molecules produced per molecule of NO<sub>x</sub> consumed, as defined by Lin *et al.* [1988]) has a mean value of 5.5 in the U.S. boundary layer and is more than 2 times higher in the western United States (9.1) than in the east (4.2) because of lower NO<sub>x</sub> concentrations in the west. (Notice the slight changes of the values of O<sub>3</sub> production rate and net O<sub>3</sub> production efficiency from Jacob *et al.* [1993b], after correcting an error in saving those values.) Only 30% of the net O<sub>3</sub> production in the U.S. boundary layer in the model is deposited to the region; the remaining 70% is exported to the global atmosphere. This export amounts to about one fifth of

**Table 1.** O<sub>3</sub>-CO Correlations at North American Sites in Summer

Site	Location	Period	n	Observation, Model				Reference
				Median		$\Delta O_3/\Delta CO$ , v/v	$r^2$	
				O <sub>3</sub> , ppb	CO, ppb			
<i>Flatland</i>								
Harvard Forest, Massachusetts	42°N, 72°W	June to Aug. 1990–1992	100	53	151	0.28 ± 0.02	0.78	J. Munger (unpublished data, 1993)
Scotia, Pennsylvania	41°N, 78°W	July to Aug. 1988	96	51	149	0.29 ± 0.02	0.81	D. Parrish et al. (unpublished data, 1989)
				73	212	0.28 ± 0.03	0.43	
Kinterbish, Alabama	32°N, 88°W	June to July 1990	28	67	197	0.32 ± 0.02	0.84	D. Parrish et al. (unpublished data, 1991)
				60	172	0.32 ± 0.05	0.57	
				64	159	0.41 ± 0.06	0.32	
<i>Mountaintop</i>								
Shenandoah National Park, Virginia	39N, 79W, 1100 m	June to Aug. 1989	155	41	206	<i>a</i>	0.09	<i>Poulida et al.</i> [1991]
Niwot Ridge, Colorado	40N, 105W, 3100 m	July to Aug. 1989	40	63	176	0.31 ± 0.03	0.56	D. Parrish et al. (unpublished data, 1990)
				51	121	0.15 ± 0.02	0.50	
				65	131	0.18 ± 0.01	0.77	
<i>Marine</i>								
Seal Island, Canada	43N, 66W	July to Aug. 1991	527	36	118	0.25 ± 0.01	0.77	<i>Parrish et al.</i> [1993] <sup>c</sup>
Sable Island, Canada	44N, 60W	July to Aug. 1991	1098	40	130	0.30 ± 0.01 <sup>b</sup>	0.63	<i>Parrish et al.</i> [1993] <sup>c</sup>
				36	107	0.30 ± 0.01	0.73	
Cape Race, Canada	47N, 53W	July to Aug. 1991	1035	38	123	0.31 ± 0.02 <sup>b</sup>	0.59	<i>Parrish et al.</i> [1993] <sup>c</sup>
				29	116	0.21 ± 0.01	0.47	
				35	125	0.26 ± 0.02 <sup>b</sup>	0.53	

Observation statistics are computed from hourly average data; for flatland and mountaintop sites, only data in the time window of 1300–1700 LT and with NO<sub>x</sub>/NO<sub>y</sub> < 0.3 are used (see text). Model statistics are computed from output sampled every 4 hours (model time step), in the 1300–1700 LT window for continental sites, and at all times of day at marine sites.

<sup>a</sup>Observed O<sub>3</sub> and CO concentrations are not correlated.

<sup>b</sup>Model correlations are computed for marine sites after removing points with O<sub>3</sub> less than 35 ppb and CO less than 120 ppb (background conditions), to focus on the pollution signal.

<sup>c</sup>September data reported by Parrish et al. are not included in the statistics.

the cross-tropopause transport of O<sub>3</sub> over the entire northern hemisphere in summer, implying that O<sub>3</sub> produced in the United States makes a significant contribution to tropospheric O<sub>3</sub> on the hemispheric scale.

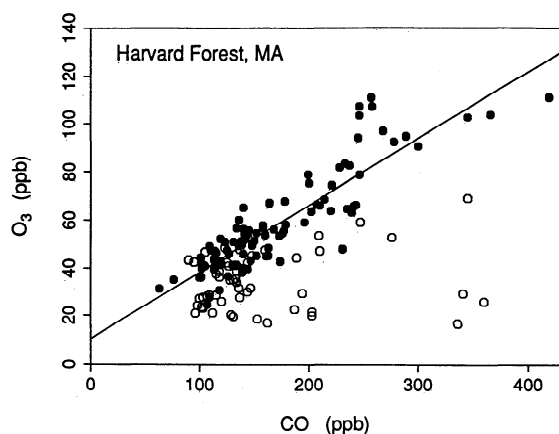
### 3. O<sub>3</sub>-CO Correlations

Table 1 summarizes observed and simulated O<sub>3</sub>-CO correlation statistics for eight nonurban sites in North America where at least 1 month of observations are available in summer (June to August). Site locations are shown in Figure 1. For continental sites we restrict our attention to the 1300–1700 LT window, when surface air is most likely representative of the boundary layer. Such a restriction is not needed at marine sites where we use data for all times of day. The model gives one value per day in the 1300–1700 LT window at any site, the exact hour depending on longitude (1300 LT in Colorado, 1500 LT on the East Coast of the United States); we use that value for constructing model statistics. All statistics in the model are constructed for June to August ( $n = 92$  points at continental sites;  $n = 552$  points at marine sites), even when the observations cover only a fraction of that period.

Figure 2 plots observed O<sub>3</sub> versus CO concentrations at Harvard Forest in central Massachusetts. There is no significant correlation because of a number of points with elevated CO but low O<sub>3</sub>, representing fresh pollution plumes that have not yet realized their O<sub>3</sub> production potential. Produc-

tion of O<sub>3</sub> over the United States in summer is mostly NO<sub>x</sub> limited [Trainer et al., 1987; Sillman et al., 1990b; McKeen et al., 1991; Chameides et al., 1992]; therefore realization of the O<sub>3</sub> production potential can be diagnosed by the NO<sub>x</sub>/NO<sub>y</sub> concentration ratio where NO<sub>y</sub> represents the sum of NO<sub>x</sub> and its oxidation products [Trainer et al., 1993]. Figure 3 plots the NO<sub>x</sub>/NO<sub>y</sub> concentration ratio at Harvard Forest against the standard normal distribution. Two distinctly different populations are found: NO<sub>x</sub>/NO<sub>y</sub> < 0.3 (photochemically aged rural air) and NO<sub>x</sub>/NO<sub>y</sub> > 0.3 (fresh pollution). The rural air data (solid circles in Figure 2) show a strong correlation between O<sub>3</sub> and CO concentrations ( $r^2 = 0.78$ ). This correlation is insensitive to small changes in the NO<sub>x</sub>/NO<sub>y</sub> criterion (using NO<sub>x</sub>/NO<sub>y</sub> < 0.2 as the criterion does not alter the correlation or the slope).

Figure 4 compares model results with rural observations (diagnosed by NO<sub>x</sub>/NO<sub>y</sub> < 0.3) at the five flatland and mountaintop sites listed in Table 1. The sites were chosen for the availability of concurrent observations for O<sub>3</sub>, CO, NO<sub>x</sub>, and NO<sub>y</sub>. The measurements at Shenandoah include NO and NO<sub>y</sub> concentrations but not NO<sub>2</sub> [Doddridge et al., 1992]; we estimate the NO<sub>2</sub> concentrations at that site from NO/NO<sub>2</sub>/O<sub>3</sub> photostationary steady state [Leighton, 1961], using local UV flux measurements to estimate the NO<sub>2</sub> photolysis rate constant [Madronich, 1987]. Selection of data with NO<sub>x</sub>/NO<sub>y</sub> < 0.3 is not possible in the model because NO<sub>y</sub> is not a tracer; however, it is not necessary



**Figure 2.** Hourly averaged O<sub>3</sub> and CO concentrations measured at Harvard Forest, Massachusetts, in June to August, 1300–1700 EST, 1990–1992. Solid and open circles represent hourly periods with a NO<sub>x</sub>/NO<sub>y</sub> concentration ratio less or greater than 0.3, respectively.

since urban and industrial pollution plumes are isolated in the model with the subgrid scheme.

The observations at Harvard Forest, Scotia (Pennsylvania), and Kinterbish (Alabama) show significant correlation between O<sub>3</sub> and CO concentrations, with  $\Delta O_3/\Delta CO \approx 0.3$  at all three sites (Table 1). We find excellent agreement between model and observations at Harvard Forest for O<sub>3</sub> and CO concentrations and for the associated  $\Delta O_3/\Delta CO$  (Figure 4a). The observations at Scotia are also well reproduced by the model, although the model has less scatter (Figure 4b). The model also reasonably agrees with the observations at Kinterbish; although the slope in the model is somewhat higher than in the observations (Figure 4c), they overlap within the standard error. The model does not, in general, capture the extremes in the observed concentrations, in part because of spatial averaging on the  $4^\circ \times 5^\circ$  grid scale.

Results for Shenandoah National Park, Virginia (mountaintop site, 1100 m altitude) are shown in Figure 4d. The observations show no significant O<sub>3</sub>-CO correlation, while the model shows a strong correlation with slope  $\Delta O_3/\Delta CO \approx 0.3$ . The median concentration of O<sub>3</sub> in the model is 22 ppb higher than observed, while the median concentration of CO is 30 ppb lower. Model statistics are for the lowest layer (0–500 m altitude) to account for the upslope circulation in the daytime [Poulida *et al.*, 1991]; however, model results in layer 2 (corresponding to the actual altitude of the site) are not significantly different. The observations are from the summer of 1989, which was unusually cold, cloudy, and rainy; mean O<sub>3</sub> concentrations at the site that summer were 10 ppb lower than the average for the past six summers [Poulida *et al.*, 1991].

Results for Niwot Ridge, Colorado (3100 m) are shown in Figure 4e. The observations at Niwot Ridge sample, in general, either relatively clean air advected from the west or boundary layer air transported upslope from the east and contaminated by the Denver metropolitan area [Parrish *et al.*, 1990]. The O<sub>3</sub>-CO correlation in the observations is driven by the Denver plume. We show in Figure 4e model results for air at the altitude of Niwot Ridge (open squares) and for the 4- to 8-hour-old Denver plume resolved with the subgrid scheme (open triangles). Model results seem consis-

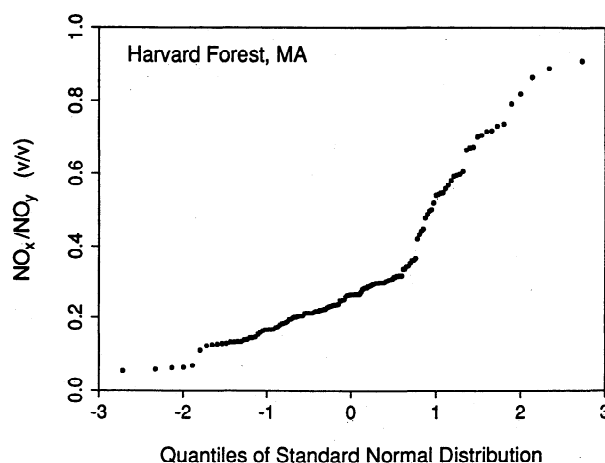
tent with observations. We find that  $\Delta O_3/\Delta CO$  at Niwot Ridge is markedly lower than at rural eastern U.S. sites, both in the observations and in the model (Table 1). This result can be explained by the low NO<sub>x</sub>/CO emission ratio in the Denver metropolitan area (0.14) as compared to the average for the eastern United States (0.23) [EPA, 1989]. The low NO<sub>x</sub>/CO emission ratio in Denver reflects the dominance of mobile sources and fuel-rich combustion in automobiles not tuned to the local altitude of 1600 m [Parrish *et al.*, 1991].

Figure 5 compares model and observations at three Canadian marine sites [Parrish *et al.*, 1993]. These sites are downwind of the northeastern United States in the prevailing summertime circulation [Wendland and Bryson, 1981]. The observations indicate  $\Delta O_3/\Delta CO$  in the range of 0.21 to 0.30, similar to values at eastern U.S. sites (Table 1). Model results are in good agreement. The variance in the model is far less than observed, certainly in part because aged pollution plumes are forced to dilute on the  $4^\circ \times 5^\circ$  grid scale (no cross-gridbox advection is allowed for subgrid plumes in the model).

Our analysis indicates that  $\Delta O_3/\Delta CO \approx 0.3$  is a uniform characteristic of boundary layer air over eastern North America in summer. Data for the free troposphere from the Arctic Boundary Layer Expeditions (ABLE) 3A and 3B [Harriss *et al.*, 1992, 1994] are generally consistent with this result. Wofsy *et al.* [1992] measured  $\Delta O_3/\Delta CO$  in the range 0.17–0.62 at 3–6 km altitude during an ABLE 3A flight along the eastern seaboard from Maine to Virginia. They measured a negative  $\Delta O_3/\Delta CO$  below 1.5 km on the same flight, evidently due to O<sub>3</sub> deposition. Data from ABLE 3B show  $\Delta O_3/\Delta CO$  in the range 0.20–0.69 for anthropogenic pollution plumes sampled in the free troposphere over eastern Canada [Mauzerall *et al.*, 1993].

#### 4. Interpretation

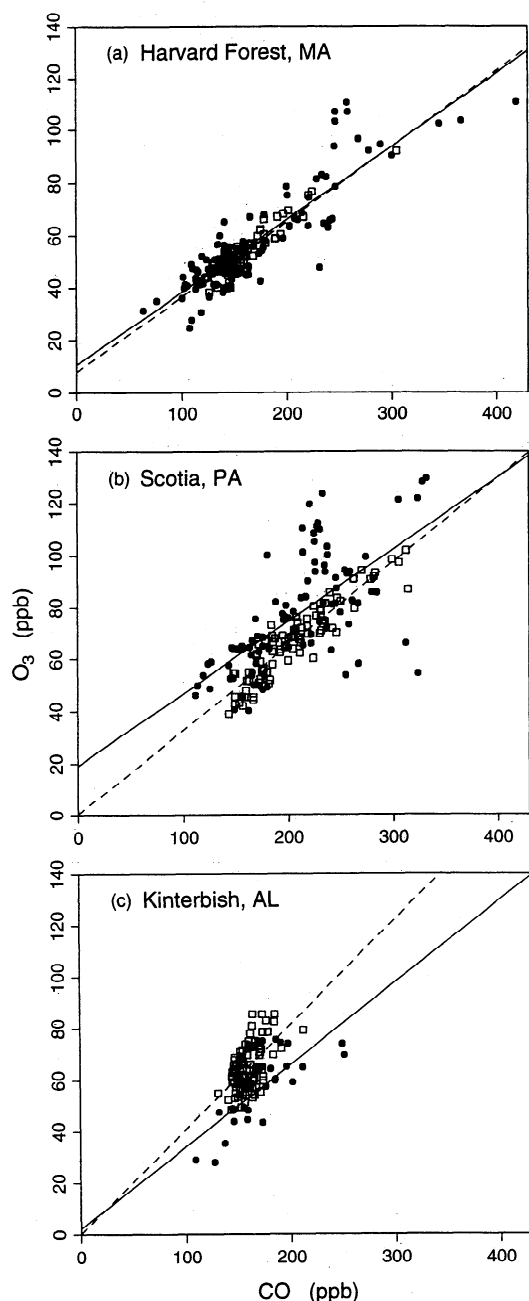
We have shown that the three-dimensional model of Jacob *et al.* [1993a] reproduces closely the O<sub>3</sub>-CO correlation and slope  $\Delta O_3/\Delta CO$  for all available sites in North America except Shenandoah National Park. This finding, combined with the generally good simulation of O<sub>3</sub> and CO concentra-



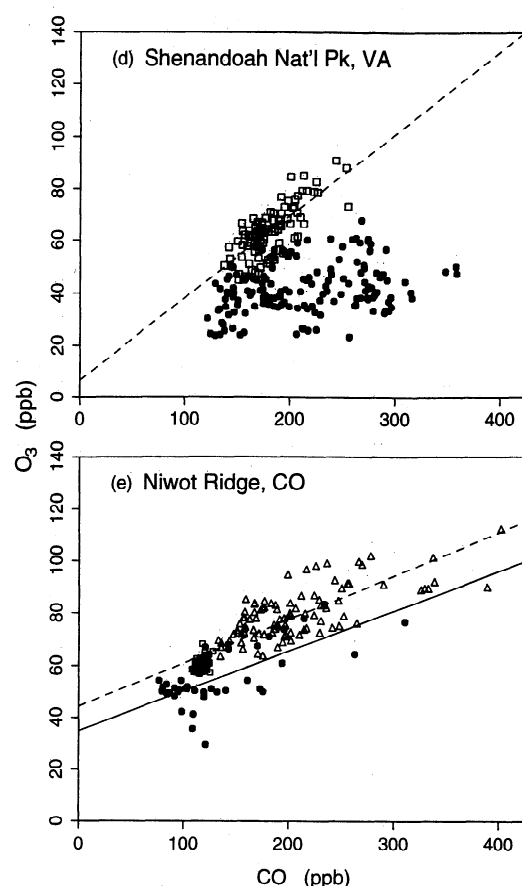
**Figure 3.** The NO<sub>x</sub>/NO<sub>y</sub> concentration ratio measured at Harvard Forest (for the same time period as in Figure 2) plotted against the standard normal distribution.

tions, lends confidence in the ability of the model to compute anthropogenic production of O<sub>3</sub> over the United States and the export of O<sub>3</sub> to the global atmosphere. Detailed discussion of model results, including O<sub>3</sub> budgets, is given by Jacob *et al.* [1993b].

We evaluate here the potential for a more direct interpretation of  $\Delta\text{O}_3/\Delta\text{CO}$  as an O<sub>3</sub>/CO anthropogenic enhancement



**Figure 4.** Observed and simulated O<sub>3</sub> and CO concentrations at five U.S. sites: (a) Harvard Forest, Massachusetts; (b) Scotia, Pennsylvania; (c) Kinterbish, Alabama; (d) Shenandoah National Park, Virginia; and (e) Niwot Ridge, Colorado. Details of the data are given in Table 1. Solid circles are observations and open squares are model values. In Figure 4e, model results are shown also for the aged Denver plume sampled with the sub-grid-nested scheme (open triangles). Lines are linear regressions to the observations (solid) and to the model results (dashed).

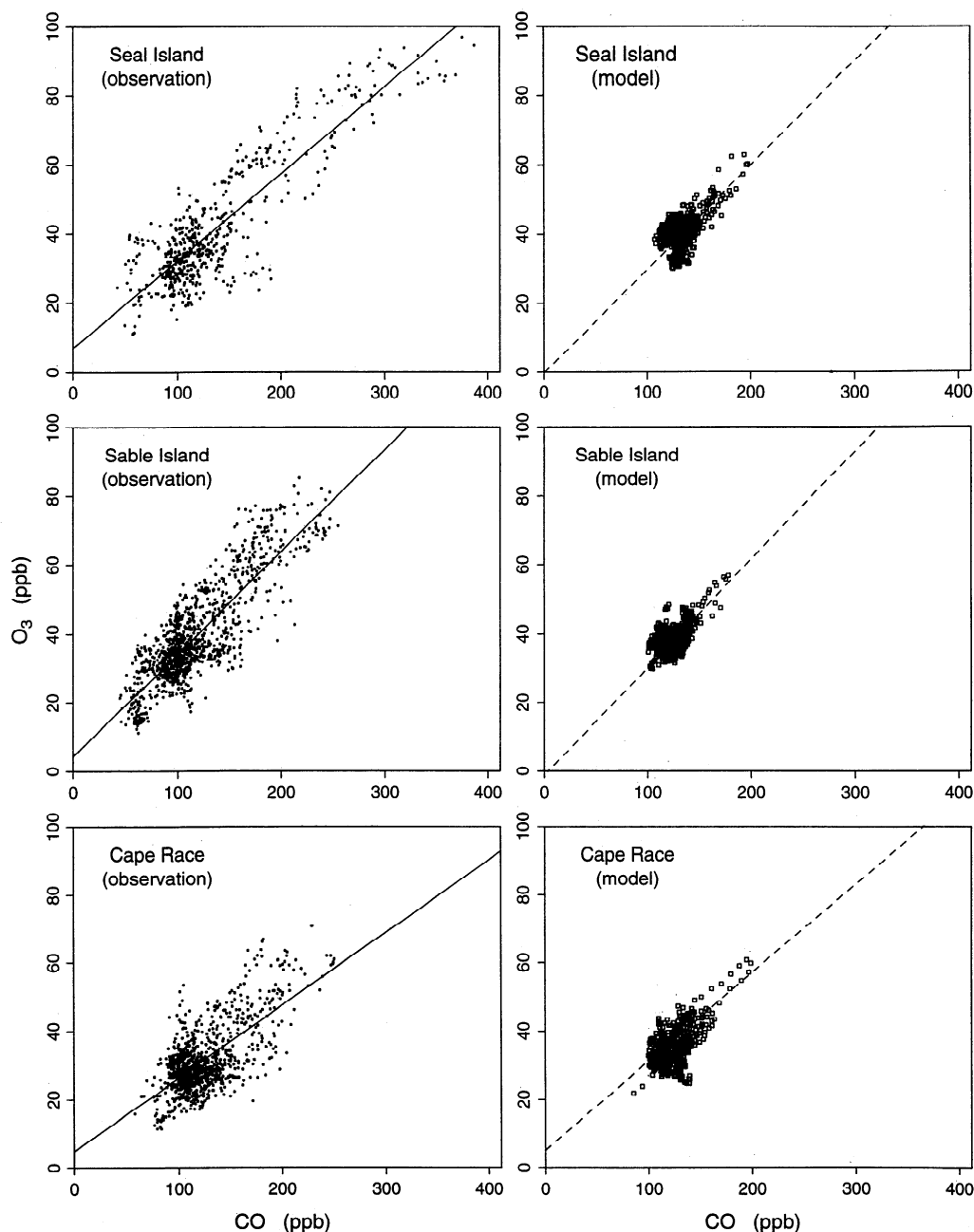


**Figure 4.** (continued)

ratio. Parrish *et al.* [1993] previously used this interpretation to estimate the export of O<sub>3</sub> from the United States to the North Atlantic. They multiplied the observed  $\Delta\text{O}_3/\Delta\text{CO} \approx 0.3$  at the Canadian marine sites of Table 1 by a CO emission inventory for the United States east of Mississippi River (approximately east of 92°W) and inferred an export flux of 1.1 Gmol d<sup>-1</sup> for anthropogenic O<sub>3</sub> out of the eastern United States (mostly, they assumed, to the North Atlantic). We find however in the model an export flux of 1.6 Gmol d<sup>-1</sup> for anthropogenic O<sub>3</sub> out of the same region; this flux is 45% higher than estimated by Parrish *et al.* [1993], even though  $\Delta\text{O}_3/\Delta\text{CO}$  in the model is indistinguishable from the observations. There are two principal reasons for the difference, as discussed below.

First, the scaling of  $\Delta\text{O}_3/\Delta\text{CO}$  as done by Parrish *et al.* [1993] could be improved by accounting for chemical sources and sinks of CO in addition to direct emission. Table 2 gives an inventory of CO sources and sinks for the continental boundary layer of the eastern United States in the three-dimensional model. Direct emission represents only 60% of the total CO source; the balance is contributed by atmospheric oxidation of hydrocarbons, in particular isoprene (20%). This chemical source is compensated by a strong chemical loss, reflecting the high concentrations of both CO and OH over the eastern United States. Overall, the net source of CO in the boundary layer of the eastern United States is 18% higher than the emission flux.

A more fundamental difficulty in interpreting observed  $\Delta\text{O}_3/\Delta\text{CO}$  as an O<sub>3</sub>/CO anthropogenic enhancement ratio is that in the absence of photochemistry, O<sub>3</sub> would be nega-



**Figure 5.** Observed and simulated O<sub>3</sub> and CO concentrations at three Canadian marine sites (Table 1). Lines are linear regressions.

tively correlated with CO due to deposition. As a result, the measured  $\Delta\text{O}_3/\Delta\text{CO}$  is less than the actual anthropogenic enhancement ratio. We determined the magnitude of this effect by conducting a model simulation with O<sub>3</sub> concentrations regulated solely by advection of boundary conditions and deposition (no chemical production or loss). Figure 6 shows the results for Seal Island, Canada; without photochemistry, O<sub>3</sub> and CO concentrations are negatively correlated (crosses, top panel). We can define an O<sub>3</sub> photochemical enhancement as the difference between the O<sub>3</sub> concentrations in the standard simulation and those in the simulation including no chemistry. This photochemical enhancement of O<sub>3</sub> shows a strong positive correlation with CO (solid squares, bottom panel). The slope in the bottom

panel (0.40) gives the actual O<sub>3</sub>/CO enhancement ratio from U.S. pollution; it is 33% higher than  $\Delta\text{O}_3/\Delta\text{CO}$  in the top panel (0.30).

We now turn to the application of  $\Delta\text{O}_3/\Delta\text{CO}$  as a measure of the O<sub>3</sub> production efficiency. *Liu et al.* [1987] pointed out that the O<sub>3</sub> production is best referenced to the loss of NO<sub>x</sub> or, on a regional scale, the emission of NO<sub>x</sub>, since O<sub>3</sub> production is NO<sub>x</sub> limited. A net O<sub>3</sub> production efficiency  $\epsilon_N$  was defined by *Lin et al.* [1988] as the net number of O<sub>3</sub> molecules produced per NO<sub>x</sub> molecule consumed. By scaling the observed  $\Delta\text{O}_3/\Delta\text{CO}$  in photochemically aged air to a CO/NO<sub>x</sub> source ratio, we can obtain an estimate of the net O<sub>3</sub> production efficiency  $\epsilon_N$ ; such an estimate is however a lower limit because of deposition of O<sub>3</sub>. The CO/NO<sub>x</sub> source

ratio for the eastern United States, as defined in Figure 1, is 5.6 (using the net CO source in Table 2 and the NAPAP emission inventory for NO<sub>x</sub>). From  $\Delta\text{O}_3/\Delta\text{CO} = 0.3$ , we obtain a net O<sub>3</sub> production efficiency  $\varepsilon_N$  of 1.7 in eastern U.S. boundary layer. In comparison a value of 8.5 for  $\varepsilon_N$  at Scotia and at Egbert, Ontario, was estimated by *Trainer et al.* [1993] using observations of  $\Delta\text{O}_3/\Delta(\text{NO}_y - \text{NO}_x)$ , and *Olszyna et al.* [1993] found a  $\varepsilon_N$  value of 12 at Tennessee using the same relationship; these values would be upper limits for  $\varepsilon_N$  because of rapid HNO<sub>3</sub> deposition. Our three-dimensional model gives a mean value  $\varepsilon_N = 4.2$  for the eastern United States [*Jacob et al.*, 1993b], which is intermediate between the lower and the upper limits imposed by the observations of  $\Delta\text{O}_3/\Delta\text{CO}$  and  $\Delta\text{O}_3/\Delta(\text{NO}_y - \text{NO}_x)$ .

We have seen that deposition of O<sub>3</sub> is an important factor limiting the potential for simple interpretation of the O<sub>3</sub>-CO correlation in terms of O<sub>3</sub> production. Model results indicate that this effect is greatest in the central United States, where O<sub>3</sub> concentrations would be at a minimum in the absence of photochemistry because of the long fetch in the continental boundary layer [*Jacob et al.*, 1993a]. Figure 7 shows O<sub>3</sub>-CO correlations for the Oregon, Nebraska, Illinois, and Massachusetts grid boxes; there is no significant correlation between O<sub>3</sub> and CO in the Nebraska grid box. By subtracting the O<sub>3</sub> concentration computed in the absence of photochemistry (as in Figure 6), we obtain a strong correlation between O<sub>3</sub> photochemical enhancement and CO (solid squares in Figure 7). The slope of the linear regression analysis of the O<sub>3</sub> photochemical enhancement versus CO falls within a narrow range (0.33 to 0.49) for the four grid boxes in Figure 7 and is actually highest in the Nebraska grid box.

## 5. Conclusion

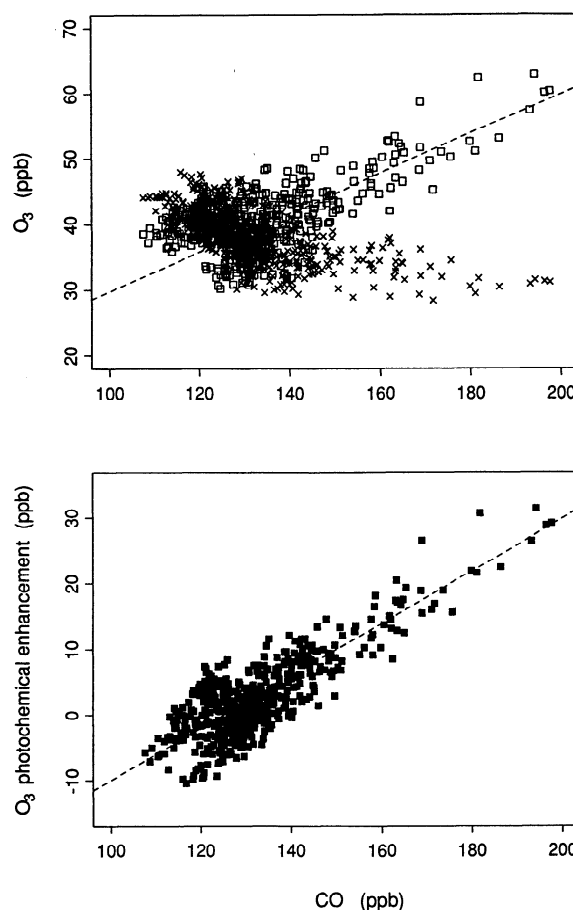
Observations at nonurban sites in eastern North America show a strong correlation between O<sub>3</sub> and CO concentrations in photochemically aged air (as defined by NO<sub>x</sub>/NO<sub>y</sub> < 0.3). The slope,  $\Delta\text{O}_3/\Delta\text{CO}$ , has a remarkably uniform value of about 0.3. Observations at Niwot Ridge, Colorado, indicate  $\Delta\text{O}_3/\Delta\text{CO} = 0.15$  in the aged Denver plume; this low value is attributed to the low NO<sub>x</sub>/CO emission ratio in the Denver metropolitan area.

The O<sub>3</sub>-CO relationship provides a sensitive test of O<sub>3</sub> production in chemical transport models. We used it to test

**Table 2.** Budget of CO for the Boundary Layer of the Eastern United States

	Rate, Gmol d <sup>-1</sup>
<i>Sources</i>	
Anthropogenic emission	3.3
Oxidation of isoprene	1.1
Oxidation of anthropogenic NMHCs	0.5
Oxidation of CH <sub>4</sub>	0.6
<i>Sink</i>	
Reaction with OH	-1.6
Net CO source	3.9

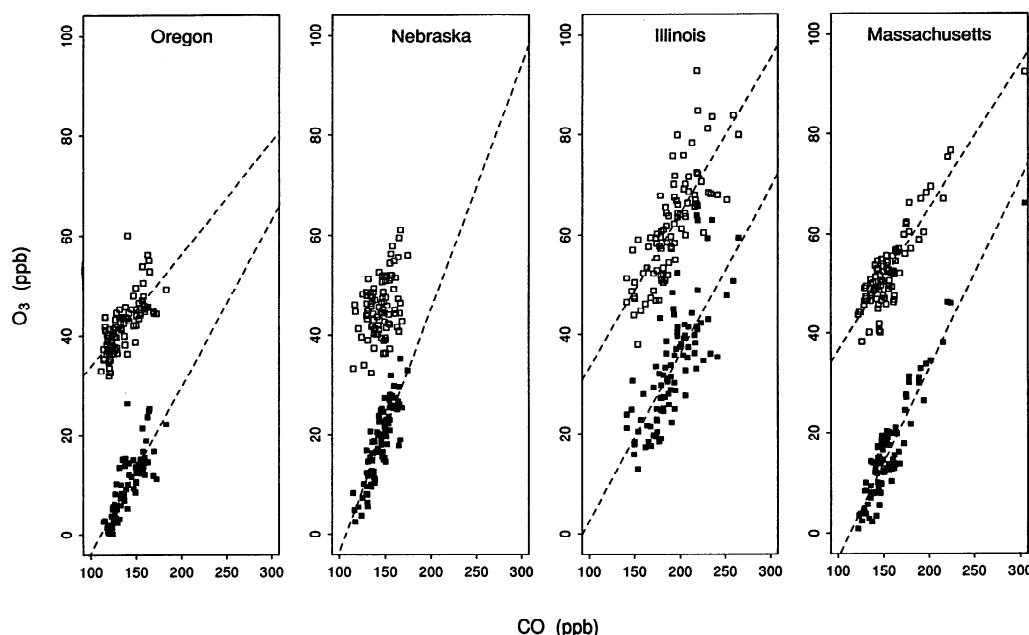
This budget is based on model results from June to August for the region enclosed by thick lines in Figure 1. Anthropogenic emission is from the National Acid Precipitation Assessment Program inventory. NMHCs, nonmethane hydrocarbons.



**Figure 6.** Simulated O<sub>3</sub> and CO concentrations at Seal Island, Canada, in the model. The top panel shows O<sub>3</sub> in the standard simulation (open squares) and in a simulation with no photochemistry (crosses); the bottom panel shows the O<sub>3</sub> photochemical enhancement defined as the difference. The lines are linear regressions to standard O<sub>3</sub> and CO (top panel) and to O<sub>3</sub> photochemical enhancement and CO (bottom panel).

a three-dimensional, continental-scale model of O<sub>3</sub> and precursors over North America [*Jacob et al.*, 1993a]. The model captures successfully the O<sub>3</sub>-CO correlations and reproduces closely the observed  $\Delta\text{O}_3/\Delta\text{CO}$ . It does not capture the full extent of variance in the observations, certainly in part because of spatial averaging on the grid scale. Simulation of the O<sub>3</sub>-CO relationship lends confidence in the ability of the model to compute photochemical production of O<sub>3</sub> over North America and its export to the global atmosphere [*Jacob et al.*, 1993b].

We investigated the possibility for a more direct interpretation of observed  $\Delta\text{O}_3/\Delta\text{CO}$  as an O<sub>3</sub>/CO anthropogenic enhancement ratio, to be multiplied by a CO source estimate for quantitative inference of photochemical O<sub>3</sub> production and export. A first complication with this simple approach is the need to account for chemical sources and sinks of CO, even in a highly polluted region such as the eastern United States. A second complication is that O<sub>3</sub> concentrations over polluted regions include a major component advected from outside the region, which is negatively correlated with CO due to deposition at the surface. As a result,  $\Delta\text{O}_3/\Delta\text{CO}$  measured at sites over the United States and downwind is



**Figure 7.** Simulated O<sub>3</sub> and CO concentrations in June to August (1200–1500 LT) for the Oregon, Nebraska, Illinois, and Massachusetts surface grid boxes. The open squares show O<sub>3</sub> concentrations from the standard simulation; the solid squares show the O<sub>3</sub> photochemical enhancement. The slopes and correlations for standard O<sub>3</sub> versus CO are Oregon, slope = 0.22,  $r^2 = 0.53$ ; Nebraska, no significant correlation ( $r^2 = 0.15$ ); Illinois, slope = 0.31,  $r^2 = 0.61$ ; and Massachusetts, slope = 0.29,  $r^2 = 0.81$ . The slopes and correlations for the O<sub>3</sub> photochemical enhancement versus CO are Oregon, slope = 0.39,  $r^2 = 0.74$ ; Nebraska, slope = 0.49,  $r^2 = 0.74$ ; Illinois, slope = 0.33,  $r^2 = 0.60$ ; and Massachusetts, slope = 0.39,  $r^2 = 0.87$ .

significantly less than the O<sub>3</sub>/CO anthropogenic enhancement ratio, and the direct interpretation of observed  $\Delta\text{O}_3/\Delta\text{CO}$  may underestimate substantially the O<sub>3</sub> production and export.

From the  $\Delta\text{O}_3/\Delta\text{CO}$  observed in the eastern United States scaled to a CO/NO<sub>x</sub> source ratio for the region, we infer a lower limit of 1.7 for the net O<sub>3</sub> production efficiency  $\varepsilon_N$  defined as the net number of O<sub>3</sub> molecules produced per molecule of NO<sub>x</sub> consumed. This value is a lower limit because of O<sub>3</sub> deposition. Observations of  $\Delta\text{O}_3/\Delta(\text{NO}_y - \text{NO}_x)$  in the eastern United States yield values of 8.5–12 for  $\varepsilon_N$ ; these values are upper limit because of rapid HNO<sub>3</sub> deposition. The mean  $\varepsilon_N$  value of 4.2 computed in the three-dimensional model for the boundary layer of the eastern United States falls within the limits imposed by the observations of  $\Delta\text{O}_3/\Delta\text{CO}$  and  $\Delta\text{O}_3/\Delta(\text{NO}_y - \text{NO}_x)$ .

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